NASA TT F-10,249

A REFRACTORY MATERIAL RESISTANT TO THERMAL SHOCK: IMPREGNATED TANTALUM CARBIDE

André Hivert

Translation of "Un matériau réfractaire résistant au choc thermique: le carbure de tantale imprégné."
Paper presented at the Conference on Materials for Use in Space, Paris, 7-11 February 1966,
Centre National d'Études Spatiales, ONERA, TP No. 323.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON SEPTEMBER 1966

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ABSTRACT

Evaluation of the refractory properties and resistance to thermal shock of sintered tantalum carbide impregnated with copper or silver at high temperatures are discussed. It was found that the process of impregnation was inhibited at temperatures of about 1100° C by a film of tantalum oxide but that, upon heating to 1750° C, the oxide film reacted with the carbon in the tantalum carbide, thus making impregnation practical. Various tests indicated that the effect of tantalum-carbide impregnation with a metal which is a good conductor of heat results in greatly improved resistance to thermal shock. While impregnation slows down the rate of oxidation in air it does not eliminate it entirely, so that the same restrictions in regard to oxidizing atmospheres apply as for graphite.

Summary

Tantalum carbide is an ultra-refractory compound (melting point 3,880° C) but its resistance to thermal shock is similar to sintered alumina. To eliminate this defect, the solution investigated here consists of the preparation by sintering of fragments of stable porosity, which are then impregnated with a metal. /1*

The "natural" sintering process of tantalum carbide was investigated with the refractometer. The influence of minor additions inhibiting the process was noted. Copper is a particularly convenient inhibitor which makes it easily possible to obtain a product with an open and stable porosity of 20 to 40 percent.

Impregnation of the specimens with silver or copper was carried out by two methods. It was shown that the refractory structure was not damaged

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*Numbers given in margin indicate pagination in original foreign text.

after this operation. It also remains unchanged during utilization. These new cermets have remarkable resistance to thermal shock. Their rate of oxidation is very much less than that of dense tantalum carbide. The porous fragments show notable mechanical strength up to as much as 3,200° C. Over the entire temperature range this characteristic is greater than that of polycrystalline graphite of identical porosity.

Introduction

As the demands on temperature resistance of materials increase, now a permanent tendency in such advanced technologies as the aerospace field, the range of choice open to the designer becomes continually narrower. Above 2000° C and where high stresses are to be anticipated, there frequently is no longer any choice and the only material available is graphite.

This situation is evidently such a cause for concern that attention has been directed for some years to refractory compounds suitable for closing this gap. Carbides occupy a predominant position among these. Specifically, tantalum carbide, with 3,880° C, together with hafnium carbide, holds the record for melting point of binary compounds. Its various physical properties have been investigated and measured (refs. 1, 2, 3). Table 1 shows the values /2 generally accepted at present. A brief look at these figures is sufficient to indicate that tantalum carbide is extremely sensitive to thermal shock due to the combination of a high modulus of elasticity and low thermal conductivity.

If we consider all the parameters involved in the expression of stresses of thermal origin, comparison of the characteristics of tantalum carbide and of alumina is particularly instructive.

Table 2 shows that there is a striking similarity between the two materials from this point of view. Alumina has a slight advantage in every other respect except that of the modulus of elasticity.

On the whole, it may be assumed that tantalum carbide will react to thermal shock almost identically as does alumina, a product with practical limits today familiar to any researcher.

The same limits in practice prevent the use of tantalum carbide for such applications as those which graphite satisfies with its practical invulnerability to thermal shock due to its satisfactory thermal conductivity (0.3 CGS) and its exceptionally low Young's modulus (1000 kg/mm^2).

Another defect of tantalum carbide is its oxidation rate which is due to the high heat of formation of tantalum oxide (500 kcal/mole) and its "powdery" character, permeable to this oxide, which does not protect the underlying zones (ref. 4). Oxidation of 1 cc of tantalum carbide releases 38 as against 4 kcal for the same volume of graphite.

TABLE 1. PROPERTIES OF TANTALUM CARBIDE.

Melting point, 3,880° C
Boiling point, 4,730 to 4,830°. C
Heat of formation, 36.8 kcal/mole
Density, 14.5
Resistivity, 25μΩ/cm
Rockwell A hardness, 89
Young modulus, 32,000 kg/mm^2
Poisson coefficient, 0.17
Thermal conductivity, 0.053 CGS
Dilatation coefficient, $8.7 \cdot 10^{-6}$
Tensile strength, 20-25 hbar

TABLE 2. COMPARISON OF PARAMETERS INFLUENCING RESISTANCE TO THERMAL SHOCK.

		TaC	Al_2O_3
Direct function	Tensile strength in hbar	25	30
	Thermal conductivity in CGS	0.053	0.069
	Thermal diffusion in CGS	0.67	0.82
Inverse function	Dilatation coefficient	$8.2 \cdot 10^{-6}$	$6.8 \cdot 10^{-6}$
	Young's modulus in hbar	32,000	40,000

This rapid examination indicates that the practical use of tantalum carbide is subordinate to prior correction of the two major defects of sensitivity to thermal shock and of oxidation rate.

The solution investigated here consists of impregnating the porous fragments of refractory carbide with a metal. An improvement may be anticipated due to the increase--probably very appreciable--of mechanical strength in relation to porous carbide, together with an increase of thermal conductivity.

Rapid calculation shows that this last parameter can be increased by a factor of 6 by using metals which are good heat conductors, such as copper or silver, at a ratio of 30 percent vol.

On the other hand, it is quite evident that we must accept a certain reduction in strength of the nonimpregnated grains in relation to the dense material. Nevertheless, the overall result should be positive.

Preparation of Porous Fragments Stable at High Temperature

By interrupting the sintering process, it is always possible to maintain a given porosity. However, the temperature of utilization in practice must then in no event exceed the maximum sintering temperature without resulting in unaccpetable contraction. It thus becomes necessary to investigate the process of sintering tantalum carbide. /3

The basic instrument of this investigation is an electric retractometer shown in figure 1.

The test specimen is introduced at one end of a graphite tube. It is flush at this end and at the other end is in contact with a graphite rod which transmits the motion due to contraction to a sliding contact moving along a wire in which flows a dc current of a few mA.

A recording potentiometer is connected between the sliding contact and one end of the wire. The sample is accurately measured before and after the experiment.

The recording allows us to measure the contraction between these two reference points. The advantages of the device are both to limit the friction to that of a blade on a wire and to be suitable for any desired amplification simply by changing the current intensity.

Figure 2 represents the retractometric diagram of a bar, 60 X 6 mm, produced by compaction under 1 ton/cm^2 of commercially available powdered tantalum carbide with a classification between 1 and 3 μ. It should be remembered that the sintering threshold lies around 1,200° C and that the process is terminated around 2,000°, even though a porosity on the order of 20 percent still subsists at this temperature.

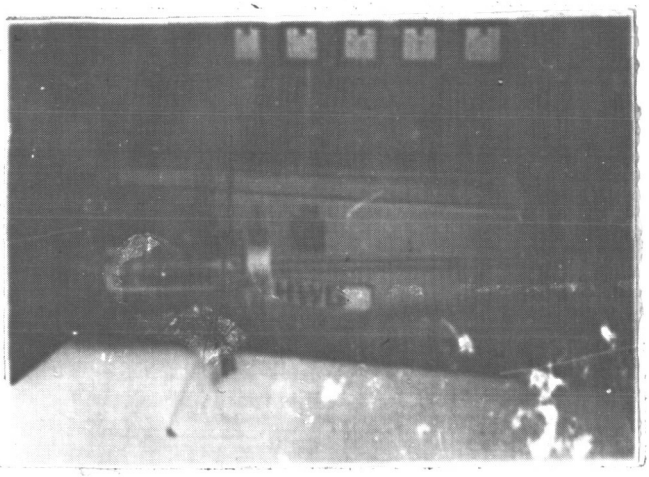


Figure 1. Electric retractometer.

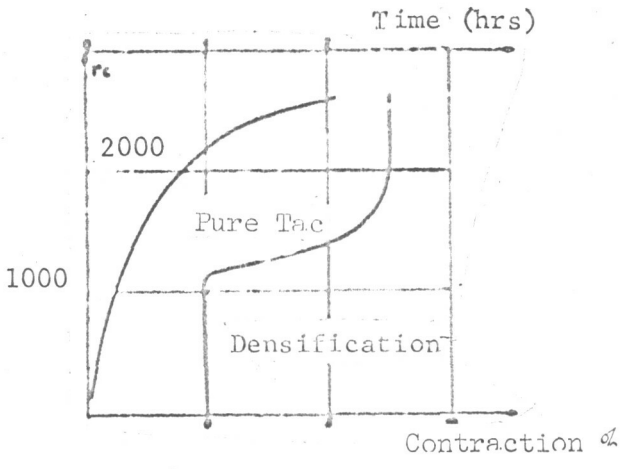


Figure 2. Retractometer diagrams of sintered tantalum carbide.

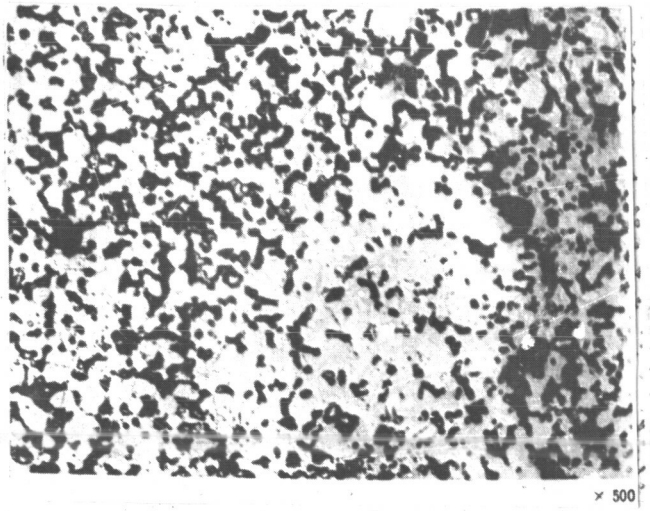


Figure 3. Microgram of tantalum-carbide fragment with sintering interrupted at 1,700° C.

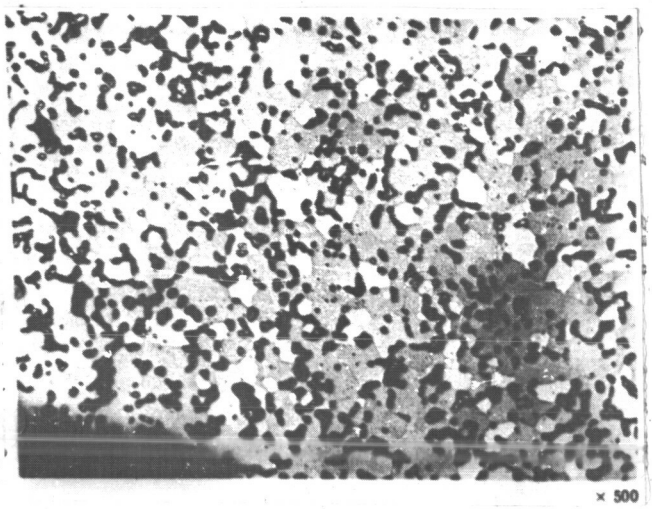


Figure 4. Microgram of tantalum-carbide fragment with sintering interrupted at 2,000° C.

The cause which blocks contraction is demonstrated by figures 3 and 4, which are metallograms of specimens where sintering was arrested at 1,700 and at 2,000° C respectively. It will be seen that a macrocrystallization process starts at 1,700° C in certain zones. The process has completely entered the fragment at 2,000° C. The reduced development of the grain surfaces is sufficient to lower densification kinetics to a negligible level. A later increase to 3,000° C yields no measurable dimensional modification.

It follows that a fragment stable at high temperature will preserve the porosity established at 2,000° C. The parameter exercising the predominant influence on this residual porosity is the density prior to sintering.

Figure 5 shows this relation graphically as a function of the compacting pressure.

It will be noted that, if we desire to attain prosities of 30 to 40 percent which are values probably required, relatively low pressures must be used which will give the compacted product a poor bonding ability.

On the other hand, the strong curve plotted in this zone suggests that /4 the inevitably unequal pressure distribution will result in highly unequal density of the sintered product. This induced us to investigate the action of minor additions on the sintering process in the hope of finding a suitable solution.

Figure 6 represents the action of nickel additions in comparison with the commercial carbide. The activating effect of nickel also reported by other authors (ref. 5) is clearly apparent not only as a function of the concentration of the adjunct but also of the manner of incorporation which produces a more or less satisfactory distribution ("ex-carbonyl," metal oxalate, nitrate).

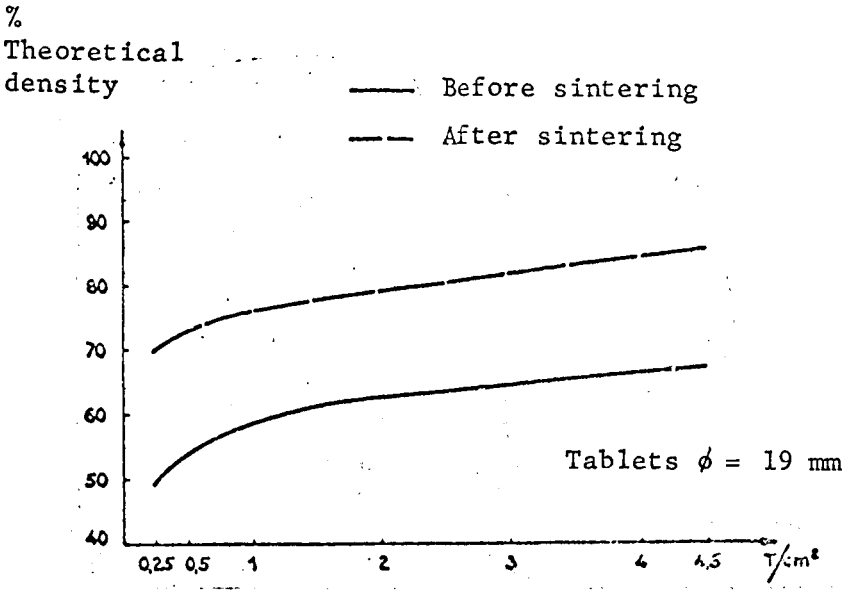


Figure 5. Relation between compacting pressure and density of tantalum carbide.

a. TaC treated HCl
b. Pure TaC
c. 0.6% Ni (Carbonyl)
d. 0.6% Ni (Oxalate)
e. 0.6% Ni (Nitrate)
f. 6% Ni (Oxalate)

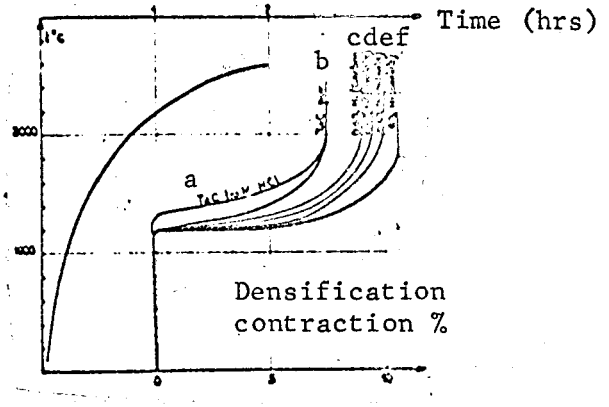


Figure 6. Retractometer diagrams showing influence of nickel content.

Washing with hydrochloric acid appreciably raises the carbide's sintering threshold. This may be due to disappearance of the traces of ferrous metals introduced in the grinding operation.

The influence of a large number of other minor additions (1 percent) was checked with the retractometer. Like nickel, others such as cobalt, iron, boron, boron carbide and beryllium carbide also exercise an activating effect.

By contrast others, including copper, silver, aluminum, manganese, columbium, silicon, tantalum and thorium are inhibitors, and thus are of particular interest since they act in the desired sense. Among them, copper has been shown to be particularly convenient in use.

a . 3% Cu
b . 3% Cu
c . 1% Cu
d . 0.5% Cu
e . Pure TaC

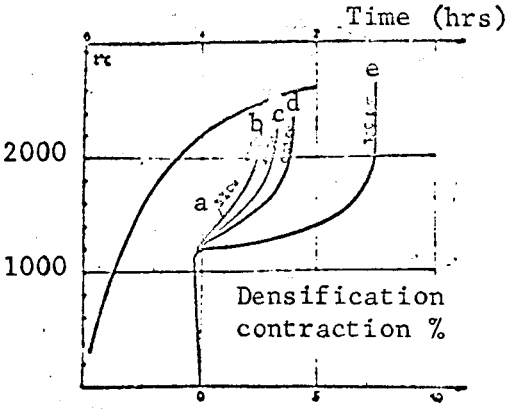


Figure 7. Retractometer diagram showing influence of addition of copper.

Figure 7 shows comparative retractograms of different additions of copper. We verified that the inhibiting effect, although very marked, does not interfere with the fundamental mechanism of sintering. It is a purely mechanical effect due to the high dilatation of the copper particles, which degrades the fragment during the first part of the heating process so that it becomes similar to a product only lightly compacted. This is the reason why the test specimens pre-sintered at 1,000° C, containing 2 percent of copper, with subsequent removal of their copper by an acid wash, always manifest the phenomenon of inhibition.

Figure 8 indicates the relation after sintering at a compacting pressure of 1 ton/cm^2, between the copper content and porosity. The curve's slope is sufficiently low so that the optimum concentration corresponding to the desired porosity does not become critical. Another advantage resulting from the use of copper as an inhibitor is to increase the proportion of open porosity to total porosity.

The mechanical properties of the various grains can thus be obtained as an inverse function of their porosity (fig. 9). Resistance to bending fracture drops from 15 to 5 hbar when porosity increases from 20 to 40 percent.

The preceding indicates that use of an inhibitor of suitable nature /5 and concentration makes it possible to conveniently prepare tantalum carbide fragments with a given porosity, stable at very high temperatures and with known mechanical strength when cold. They are now ready for impregnation.

Impregnation

The choice of the impregnating metal is limited by two imperative requirements and determined by a few desirable characteristics. The first requirement eliminates any affinity for carbon so as not to disturb the stoichiometry of the tantalum carbide which is the guarantee of its refractory

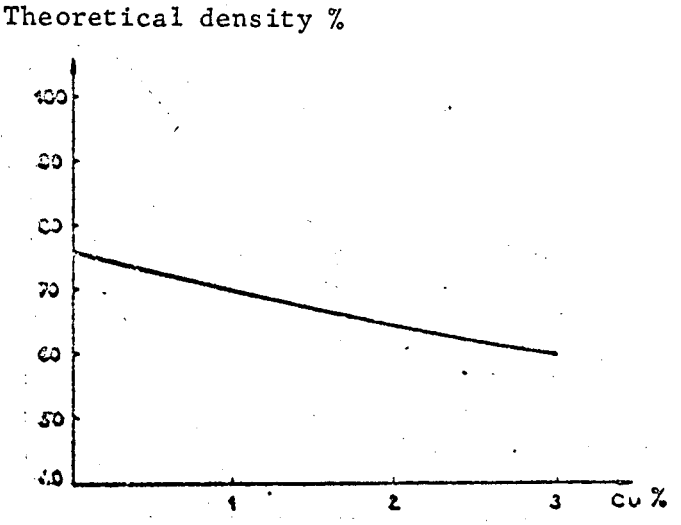


Figure 8. Influence of copper content on density after 2,500° C sintering of tantalum carbide at a pressure of 1 ton/cm^2; tablet diameter = 19 mm.

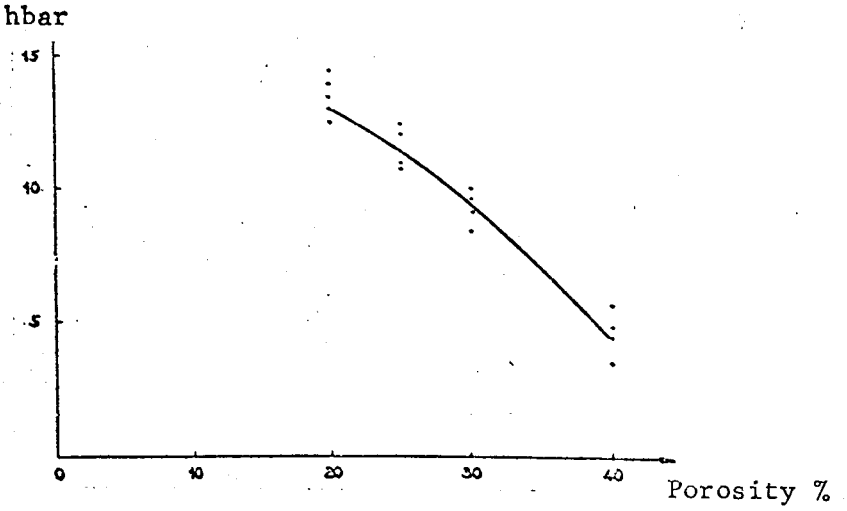


Figure 9. Influence of porosity on rupture strength under bending tests of tantulum carbide sintered at 2,500° C.

character. In this sense, the electropositive character of the metals is a criterion for initial selection. The second requirement imposes a sufficiently high "boiling temperature" so as to preserve the favorable characteristics of the metal as long as possible or at least until reduction of the thermal flow of (processing) heat to a level compatible with the inherent resistance of the grain.

TABLE 3. METAL SUITABLE FOR IMPREGNATION.

Group	Element	Oxidation potential in relation to hydrogen (volt)	Boiling temperature (°C)
3b	Indium	+0.34	2000
4b	Tin	+0.13	2270
1b	Copper	-0.337	2336
1b	Silver	-0.79	1950
1b	Gold	-1.50	2600
8	Palladium	-0.98	2200
8	Rhodium	-0.8	2500
8	Platinum	-1.2	4300

Table 3 shows the metals which were selected by virtue of these two imperative requirements. We see that with the exception of tin and indium, which are moreover less favorably placed, they are all located at the end of the series of transition elements. The additional characteristics desired are: (a) satisfactory thermal conductivity; (b) satisfactory thermal diffusion power; and (c) reasonable cost. From this point of view, copper and silver merit particular attention.

The first impregnation tests carried out with these metals consisted of liquefying them at 1,110° C in contact with porous fragments of tantalum carbide in a furnace maintained at a vacuum of 10^{-5} mm Hg. Under these conditions, if wetting occurs, capillary inhibition should occur. The results were very disappointing. Not only was there no impregnation but not even any adhesion between the metal and the fragment. The cause of the failure probably lay in the high heat of formation of the tantalum oxide, which makes the presence of an oxide film over the entire free surface of the porous grain fragment unavoidable.

In regard to wetting, this film substitutes its own characteristics /6 for those of the carbide. This is the defect which complicates brazing of refractory or inoxidizable alloys containing chrome. ONERA solved this problem in the past by exploiting the strongly deoxidizing action of saturated hydrogen-halide atmospheres (ref. 6). However, it should be pointed out that attempts at brazing tantalum were unsuccessful due to the aggressive action of such atmospheres on this metal.

In spite of this unfavorable precedent, it was reasonable to assume that the carbide would have a much lower reactivity than the free metal. Experimentation has confirmed these viewpoints. The fragments are not attacked, provided that any loss of carbon is carefully avoided by introducing into the reaction vessels graphite granules or carbon sheets. The oxide films are then very quickly destroyed so that total impregnation of small pieces by such metals as copper, silver, gold, tin or indium could be effected under remarkably quick and simple conditions.

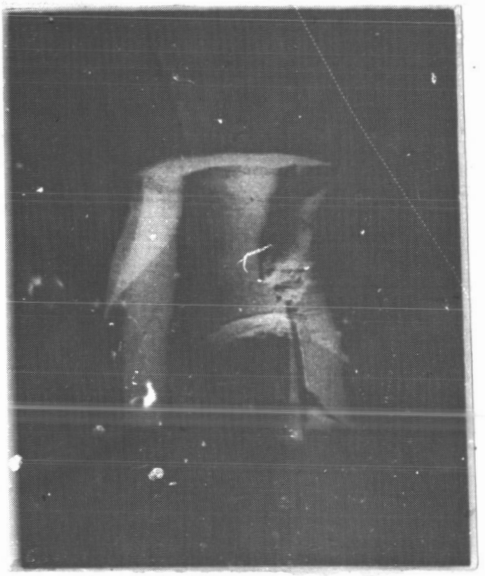


Figure 10. Example of impregnating defect.

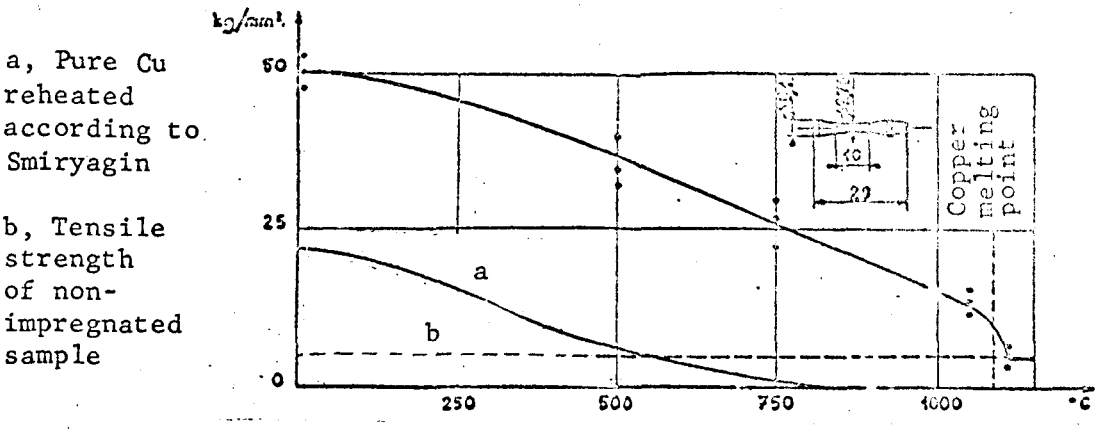
Unfortunately, when we attempt to impregnate large pieces, the astonishing deoxidizing properties of the halogenated atmospheres inhibit the process. By rapidly "cleaning" the peripheral zones, the latter become impregnated and thus insulate the center of the fragments. The fragment then no longer has a chance, regardless of exposure time, to have its oxide removed and become impregnated. This situation is most unfortunate since, during cooling, fracture is unavoidable due to the metal's contraction stresses. Figure 10 illustrates a defect of this type.

With these difficulties, impregnation experiments under vacuum were resumed, but by appreciably increasing the temperature. Under these conditions, the oxide films are destroyed by slow reaction with the tantalum carbide itself at the price of a very small carbon loss in the latter. It should be noted that the deoxidation process does not act preferentially on the peripheral zones since it does not involve a reducing agent introduced from the exterior.

With this method, it was possible to impregnate specimens 50 mm in diameter and 50 mm high to 100 percent by copper or silver, under exposures of 3-4 hours and temperatures between 1,250 and 1,325° C. Application of the process on a larger scale should raise no serious difficulties.

Verification of the Continued Existence of the Tantalum-Carbide Structure

The researcher's first concern is toward the possible damage which the refractory fragment may have suffered under impregnation. Such damage could be the effect of either the breaking of the bond between particles due to a certain solubility of the carbide in the metal, or microfractures due to



a, Pure Cu reheated according to Smiryagin

b, Tensile strength of non-impregnated sample

Figure 11. Tensile strength of tantalum carbide impregnated with copper (30 percent-vol).

stresses generated during cooling by the contraction of the metal in the solid state. The coefficient of dilatation of the latter is approximately twice that of tantalum carbide.

He is immediately reassured by the observation that bending-test speci- /7 mens impregnated and subsequently stripped of the metal by chemical action show the same breaking strength as before impregnation. Tensile-strength tests satisfactorily confirm this initial finding. Figure 11 gives the curve of breaking strength as a function of the temperature of small toric specimens of tantalum carbide with 30 percent porosity impregnated by copper. We find that the inherent strength of the fragment when cold is multiplied by a factor of 10. Beyond the melting point of copper we find this strength in the same degree.

In the interval, it should be noted that the metal contributes appreciably to the solidity of the structure, even in a temperature zone where the metal itself has no longer any measurable mechanical property (ref. 7). This phenomenon can be attributed to the influence of the viscous-friction forces originating in the metallic phase. This point of view is corroborated by the observation of a rise in breaking strength when the test load is applied more rapidly.

Figure 12 shows the results obtained on the same type of specimens impregnated with silver. The same remarks apply to this curve as the one above. Together they permit the conclusion that the impregnation process leaves the carbide structure undamaged. In use, however, the material will be subjected to much higher temperatures than those required for impregnation. The manifestation of a certain solubility of the tantalum carbide in copper would have catastrophic results due to its destructive effects on the grain interstices.

Investigation of this possible solubility was necessary. The means selected relate to the examination of interfaces between carbide and metal after prolonged exposure to different temperatures. They include micrography, microhardness test, and microanalysis with the electronic probe. In order to have

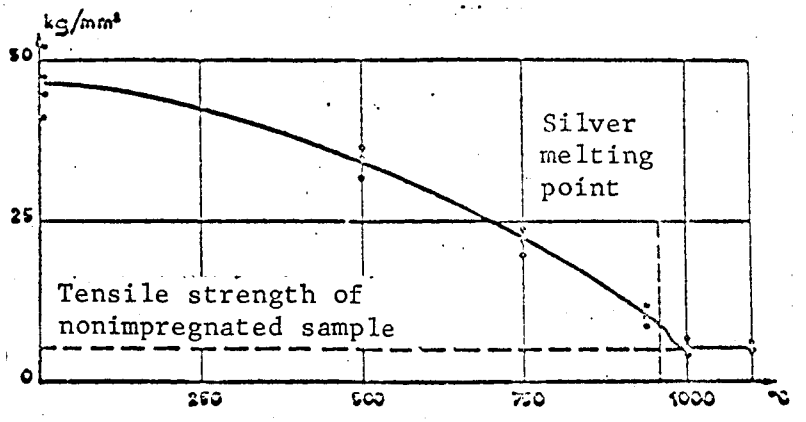


Figure 12. Tensile strength of tantalum carbide impregnated by silver (30 percent-vol).

available sufficiently large and sharp interfaces representing two very distinct domains, the investigation was carried out on dense tantalum-carbide tablets. The preparation of the tablets required the use of pressure-sintering which is the only means of achieving density (ref. 8). Figure 13 gives some data on this operation and specifically shows the contraction observed as a function of time and consequently of temperature. Contraction starts at 1,200° C, is very rapid up to 1,800° C, and subsequently slows down to become

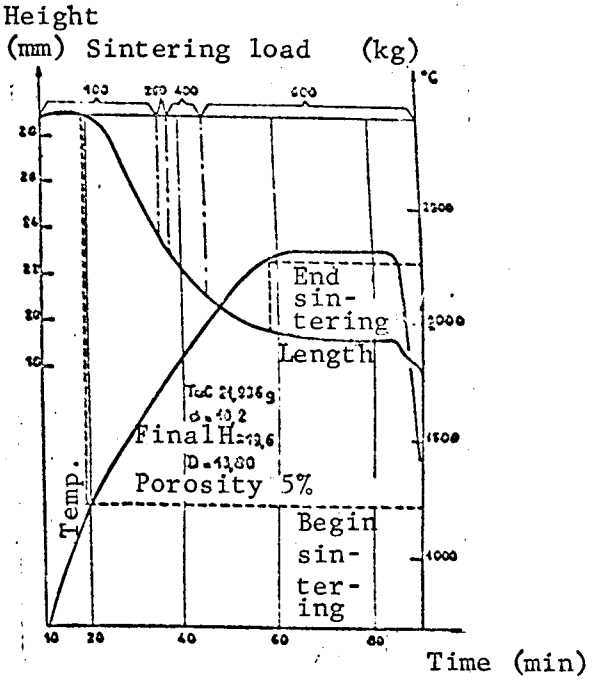


Figure 13. Pressure-sintering of tantalum carbide.

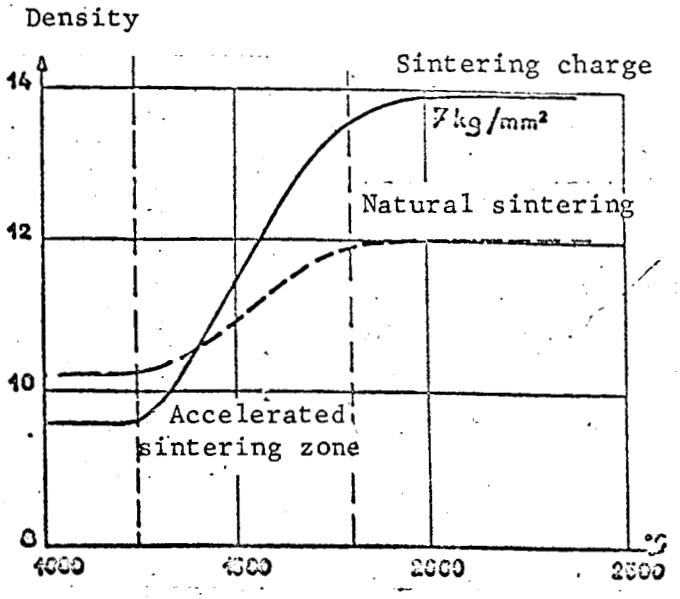


Figure 14. Comparison of two methods of sintering tantalum carbide.

negligible after 2,000° C although there still remains a "closed" porosity on the order of 5 percent.

The retractometer curves of standard and pressure sintering are not directly comparable since contraction takes place in three directions in one and in only one direction in the other case. Before comparison, they must be transposed by calculation as a function of density. Figure 14 shows the result of this operation. We are surprised to note that the accelerated sintering zone is very nearly identical for the two processes. Pressure sintering only amplifies the standard process but does not seem to involve the usual fundamental mechanism of plastic deformation. /8

Figure 15 clearly illustrates this point of view. The rise in temperature was controlled to prolong exposure duration of the tablet in the zone favorable for sintering. The residual porosity of 4.2 percent is attained at about 1,750° C. A subsequent rise up to 2,300° C under a pressure of 7 hbar does not bring about any additional contraction and, instead, an apparent expansion due to the dilatation of the testing assembly. During the experimental tests, this was the first indication of an exceptional resistance to plastic deformation of the tantalum carbide, apparently at least equivalent to that of the graphite constituting the testing assembly. Tablets so obtained were placed in contact with 5g silver or copper and raised to different temperatures for one hour in a purified-argon atmosphere.

Figure 16 shows the metallographic aspect of the interface between tantalum carbide and copper after heating to 1,800° C. The copper phase shows inclusions of high hardness which suggest dissolved and then precipitated tantalum carbide. After heating to 2,000° C, the inclusions begin to form nuclei

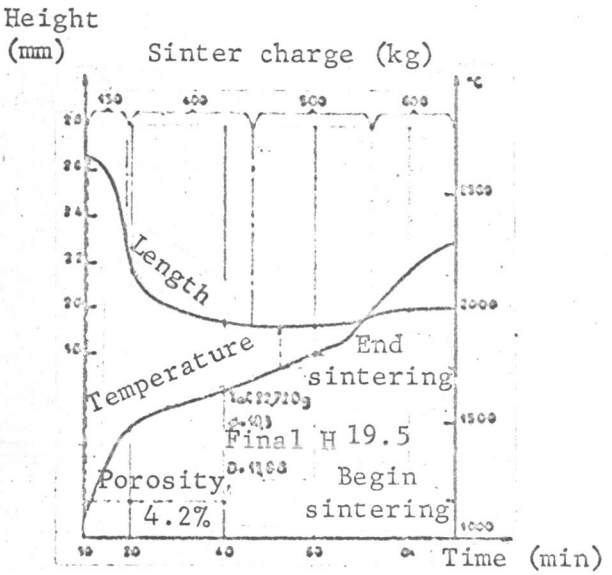


Figure 15. Pressure sintering of tantalum carbide with temperature curve added.

Figure 16. Microgram of tantalum carbide-copper interface after 1 hour at 1,800° C.

(fig. 17). At 2,100° C, the nucleus occupies the entire inclusion and its hardness and reaction to polarized light justify the comparison with graphite (fig. 18).

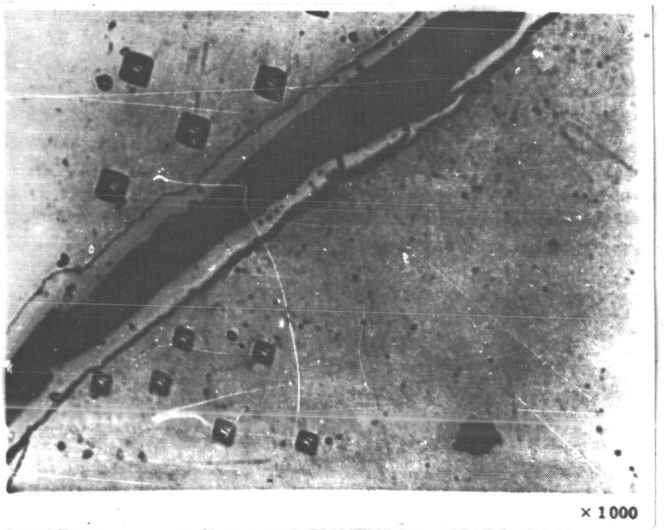


Figure 17. Microgram of inclusion in the copper phase after 1 hour at 2,000° C.

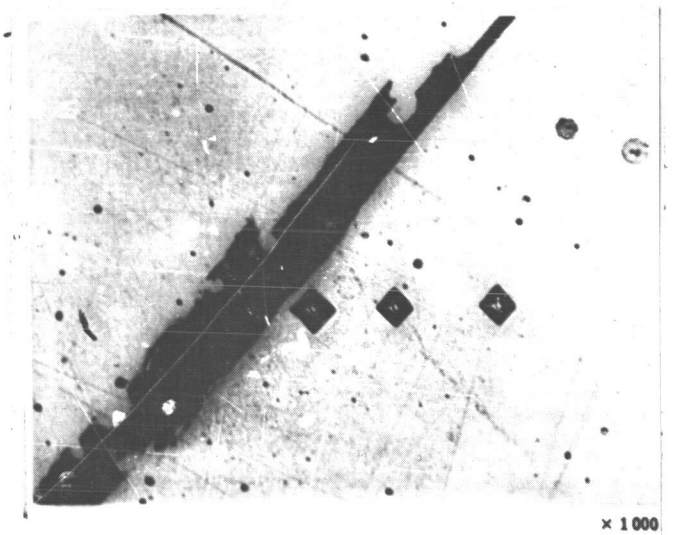


Figure 18. Microgram of inclusion in copper phase after 1 hour at 2,100° C.

Electronic microprobe analysis of precipitates obtained at 1,800° C has made it possible to identify the cation of these carbide precipitates. This is not tantalum but chromium, an impurity introduced very likely in the process of pulverization. Examination of the two domains does not show any line of tantalum in the copper or any line of copper in the tantalum carbide. Moreover, scanning perpendicular to the interface did not reveal any intermediate zone.

Under the experimental conditions, the solubility of tantalum carbide in copper appears to be zero or, in any event, is limited to a depth very much less than 1μ. The same experiments were repeated on combinations of tantalum carbide and silver. Metallographic examination does not indicate the presence of any inclusions in this case.

However, a certain heterogeneity of the metal phase is shown by the /9 microhardness. Figure 19 is a curve of statistical distribution of the hardness figures. Its asymmetry indicates a tendency toward the formation of a biphase system. However, the microprobe confirms that this second phase does not contain any tantalum carbide.

The tantalum lines are strictly absent in the silver. No intermediate phase was shown by scanning the interface. We must here again conclude on the insolubility of the tantalum carbide in the metal, at least within the instrument sensitivity limits, about 100 ppm. This investigation furnishes proof that the refractory fragment undamaged after impregnation will not be damaged during use.

Improvement Through Impregnation

a) Resistance to Thermal Shock

An electron-bombardment furnace was utilized to evaluate this important characteristic. Tantalum-carbide tablets of different porosity with a diameter of 90 mm and a height of 10 mm and impregnated with copper or silver were subjected to an electron beam focussed to accurately cover the surface of the specimen.

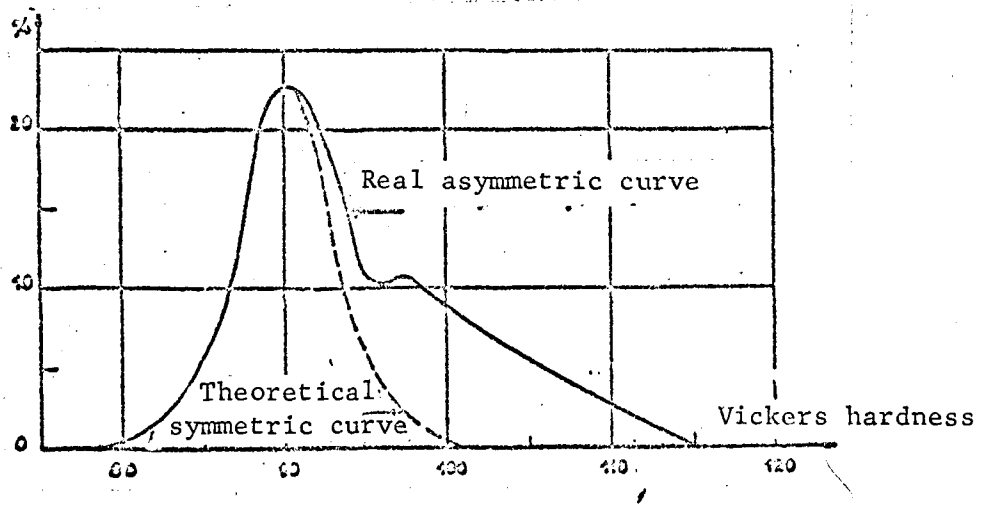


Figure 19. Statistical distribution of microhardness measurements in the silver phase of combined tantalum carbide-silver after 1 hour at 1,000° C.

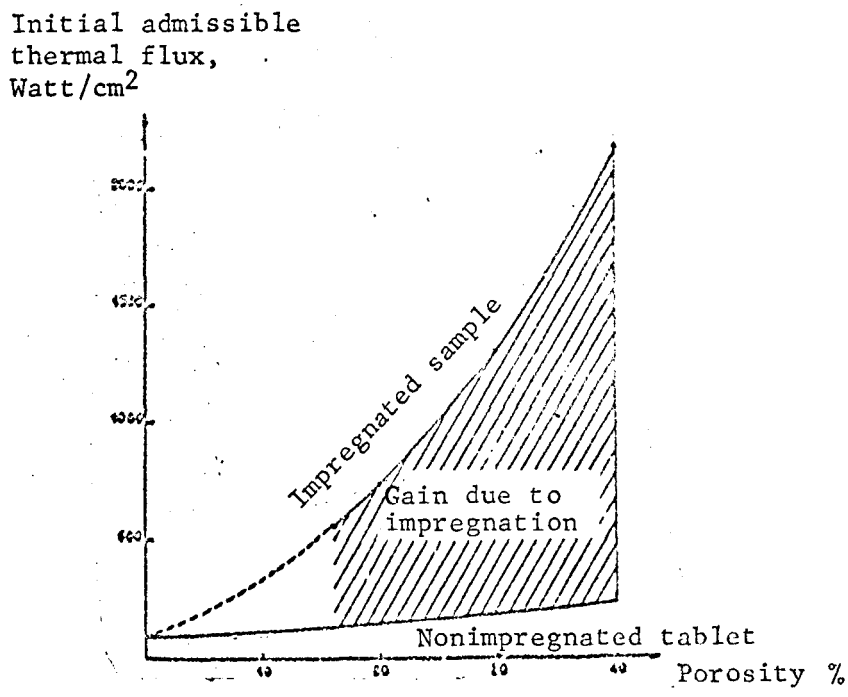


Figure 19a. Influence of impregnation with silver on thermal-shock resistance of porous tantalum-carbide fragments.

By controlling the high voltage or the temperature of the emitter filament, the overall energy of the beam is maintained at the desired level. The energy adjustment is made for copper in the cold state. Then, the specimen is put into position, the electron flow is released instantaneously, and is maintained for 10 sec. Beyond this interval, the test would no longer have any significance due to rapid volatilizing of the metal, which is a consequence of the high vacuum in the apparatus. However, it should be noted that the first seconds are the most critical from the point of view of thermal shock.

Subsequently, the tablets are examined by means of a liquation method in order to detect any possible fissures. The findings are summarized in table 4 and figure 19. The influence of impregnation with a metal of satisfactory conductivity appears decisive, even impressive, and radically modifies the character of the material.

b) Resistance to Oxidation

Figure 20 shows a comparison of the thermogravimetric curves for oxidation in air of the different specimens, e.g., of dense tantalum carbide and of 30 percent porous fragments impregnated with different metals.

It will be noted that impregnation appreciably diminishes the rate of oxidation in air without completely eliminating it. This indicates that a material of this type can be used in an oxidizing atmosphere only for relatively short periods. This restriction is also applicable to graphite.

TABLE 4. THERMAL-SHOCK RESISTANCE OF IMPREGNATED TANTALUM CARBIDE.

Fragment porosity (percent-vol)	Impregnating metal	Permissible initial thermal flow ($Watt/cm^2$)
20	none	150
20	silver	750
20	copper	750
30	none	200
30	silver	1300
30	copper	1200
40	none	220
40	silver	2200
40	copper	2000

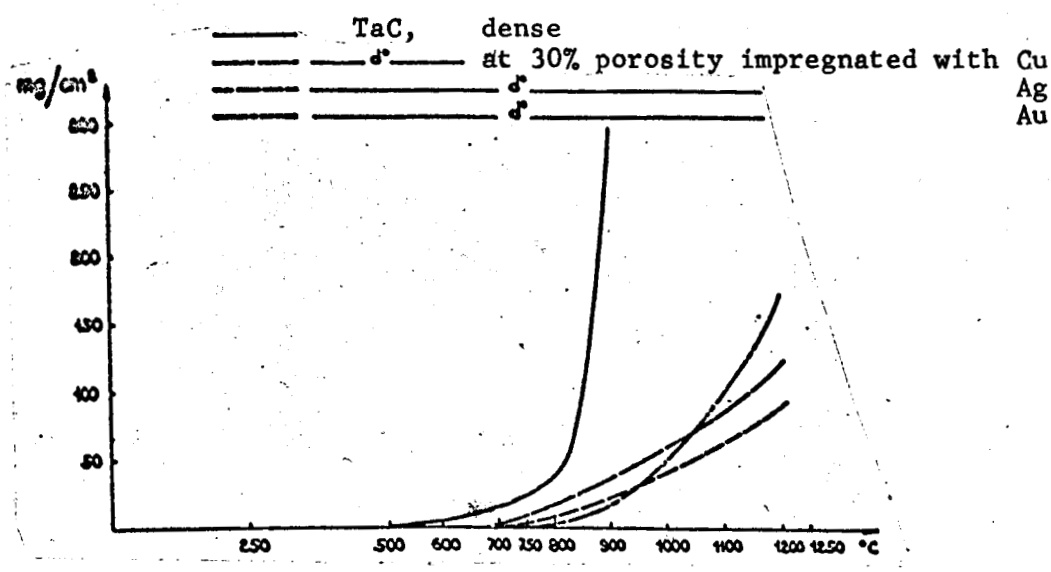


Figure 20. Oxygen fixation as a function of temperature under heating in air; rate of heating = 400°/hr.

Mechanical Properties at High Temperature of Porous Fragments

It was demonstrated that the porous fragment is not damaged either by /10 impregnation or use below the metal boiling temperature. However, beginning with the instant when the metal melts, only the tantalum-carbide fragment provides the resistance of the material. It is therefore absolutely necessary to know its mechanical properties at high temperature. The pertinent literature is almost completely silent in this respect. The only indication was found in

reference 3, which states succinctly "creep becomes very high beyond 2,200° C." To gather more information, it was decided to carry out tensile strength tests on toric specimens of nonimpregnated porous tantalum carbide.

The basic instrument of this investigation is a tensile test device, designed and constructed at ONERA, which has certain particularly valuable advantages (ref. 9)

a) an airtight housing for introducing a protective gas such as argon;

b) possibility of automatically conducting load or elongation test schedules;

c) an extensometer with large amplification in direct contact with the heads of the specimen and not in contact with the clamping device;

d) a device for mounting brittle specimens without the risk of breakage;

e) heating by means of the Joule effect with continuous and extremely sensitive voltage adjustment providing flow of currents to 1000 A and furnishing very high temperatures.

The latter are measured with the optical pyrometer by taking into account the required correction by the value of the emission power in the infrared spectrum (0.655 μ). The literature indicates 0.67 for tantalum carbide (ref. 10). The absorption by the observation window was estimated as 20° C.

Figure 21 shows the relation between the test temperature and the breaking strength. The curve passes through a maximum around 2,000° C. Since a slight elongation appears at this temperature, it may be assumed that this maximum is a consequence of the correction by plastic deformation of the device's alignment defects, which are inevitable in spite of every possible precaution.

Subsequently, the curve begins to bend and drops steeply. The apparent elastic limit is given as an indication because the inflection point of the stress elongation diagram is difficult to locate with accuracy. It should be noted that, in spite of the weakening of breaking strength beyond 2,000° C, there still subsist 3 hbar at 3,000° C and even 7 hbar when the load is applied more rapidly. At 3,200° C, the strength has still not become negligible since it was recorded at 1.8 hbar but elongation at fracture reaches 0.5 mm when the load is applied at the rate of 0.025 hbar/sec.

Figure 22 is an electronic microfractogram of a specimen which broke under these conditions. The fracture is nearly entirely intergranular and shows no evident manifestation of plastic flow. Comparison with figure 23, which shows the view of a fracture at ambient temperature, shows no fundamental differences. We merely find a larger number of flakes of the varnish which was used in making the replica in figure 22 (fracture at 3,200° C), which seems to be indicative of a certain "loosening" of the grains.

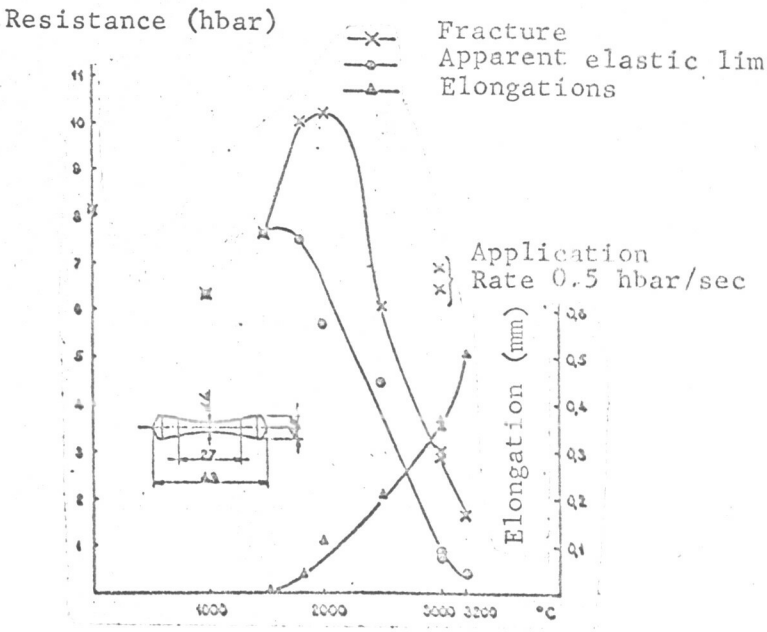


Figure 21. Mechanical properties as a function of temperature of tantalum carbide with 30 percent porosity. Application rate 0.025 hbar/sec.

Figure 22. Electronic microfractogram of test specimen of tantalum carbide fractured at 3,200° C.

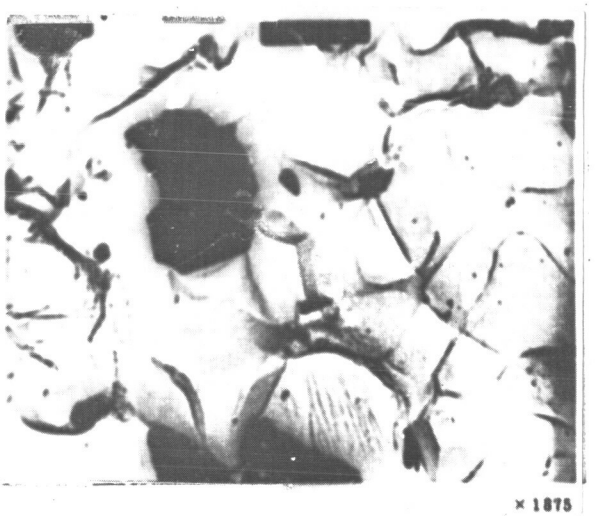


Figure 23. Microfractogram of test specimen of tantalum carbide fractured at 20° C.

Figure 24 is an oblique-section micrograph of the same test specimen. It shows the existence of fissures due to decohesion perpendicular to the direction of tensile stress, which undoubtedly contribute to elongation without explaining it entirely.

Figure 25 shows a micrograph of the specimen at a point 2 mm from the fractures. The grains are very nearly equiaxial and thus manifest no preference for deformation in the direction of tensile stress.

Figure 26 also relates to the fracture at 3,200° C and shows that a certain loss of carbon through vaporization is inevitable at this temperature. The surface zone is sufficiently impoverished of this element so that the radiocrystallogram detects the presence of the Ta_2C-phase.

To sum up, the tensile-stress tests at very high temperature on porous tantalum carbide show plastic deformation without making it possible to determine the mechanism, probably because recrystallization constantly restores the deformed system. On the other hand, they demonstrate clearly the exceptional resistance of this carbide under very severe temperature conditions.

To better judge this, it will be of interest to compare this resistance with that of identical graphite specimens tested with the same equipment. The graphite ("Carbone Lorraine 5890") was selected because it is actually one of the best grades of isotropic polycrystalline graphite available on the world market. Its calculated total porosity is about 20 percent and was therefore compared with the fragments of tantalum carbide of the same porosity.

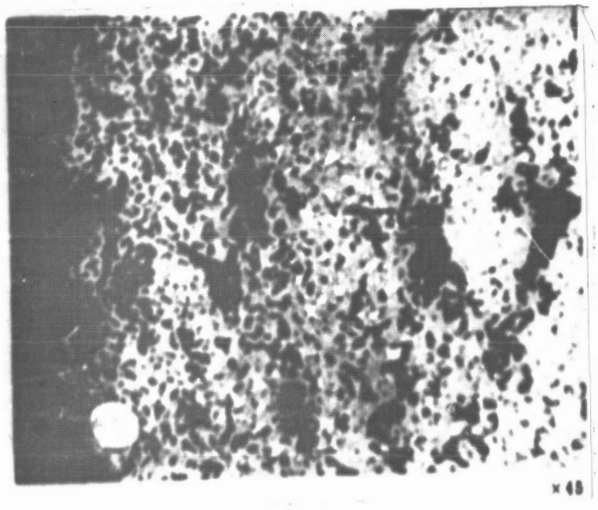


Figure 24. Oblique-section micrograph of test specimen of tantalum carbide fractured at 3,200° C.

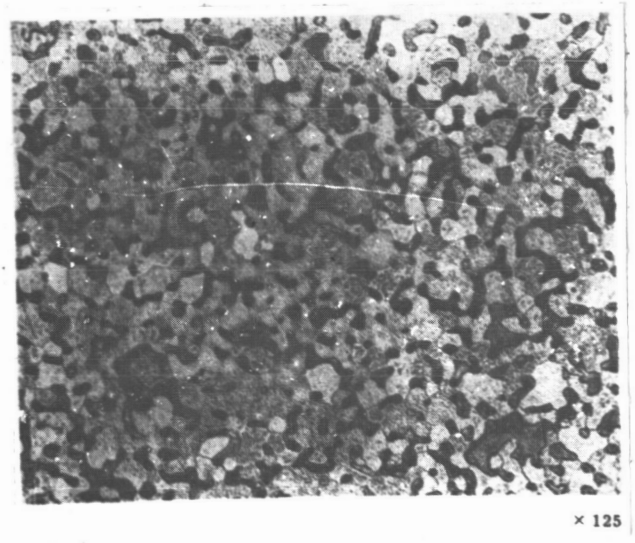


Figure 25. Micrograph of test specimen of tantalum carbide fractured at 3,200° C at a point 2 mm distant from the fracture.

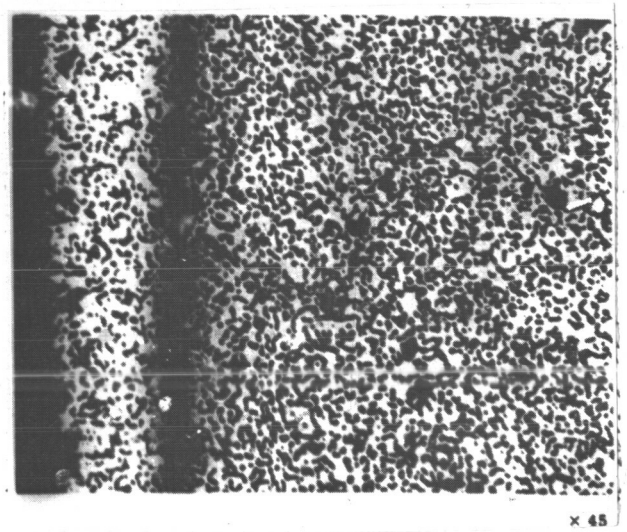


Figure 26. Microgram of test specimen of tantalum carbide fractured at 3,200° C-edge of specimen.

Figure 27 shows the rupture strength of the two materials as a function of temperature between 2,000 and 3,200° C. The superiority of tantalum carbide in this range is obvious.

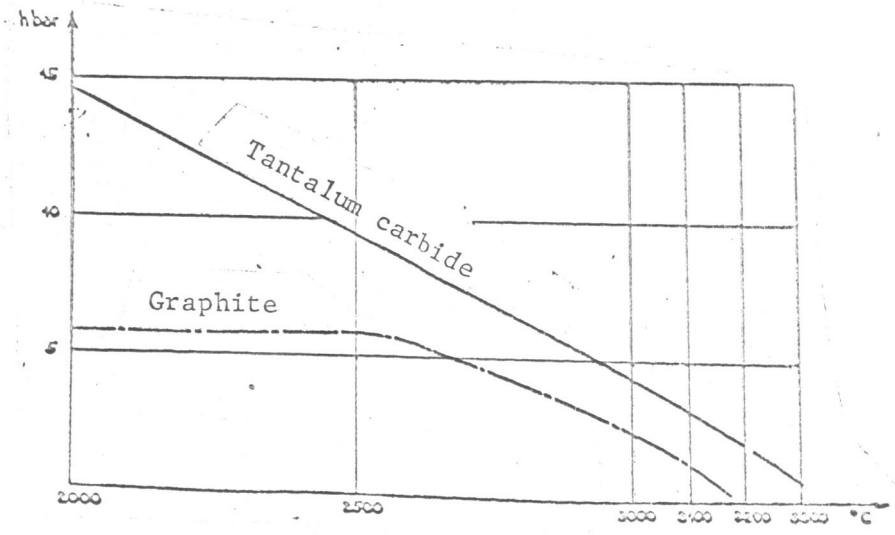


Figure 27. Comparison of tensile strength at high temperature between graphite (Carbone Lorraine 5890) and sintered tantalum carbide with 20 percent porosity; rate of application 0.025 hbar/sec.

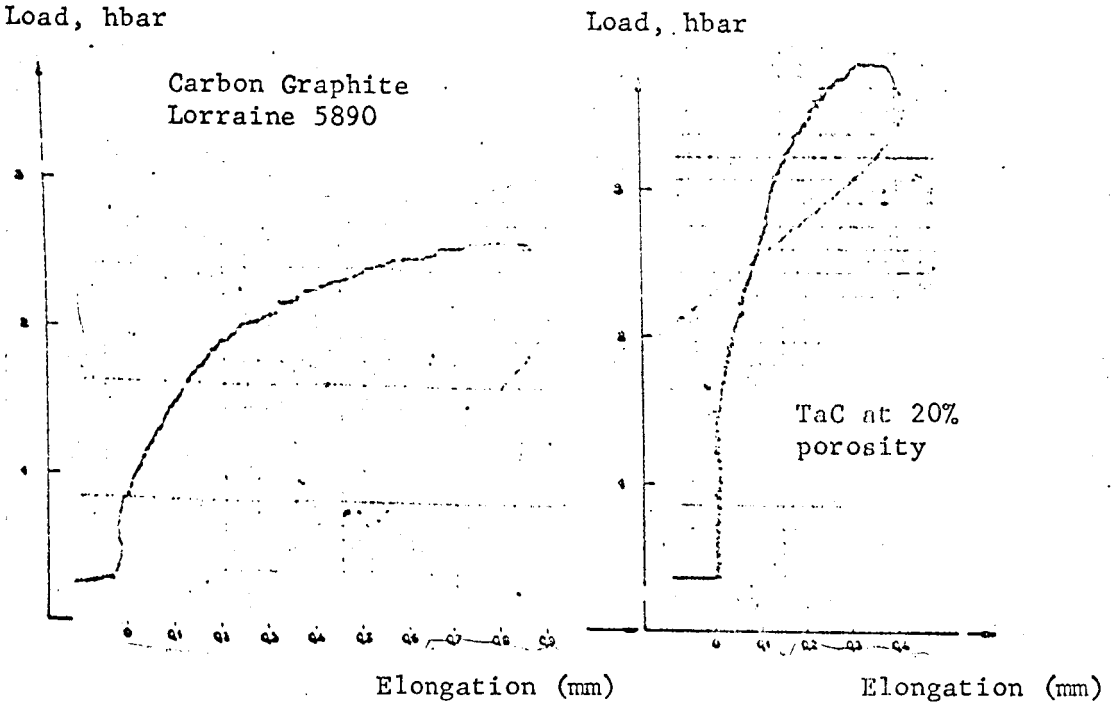


Figure 28. Diagram of strain-deformation at 3,060° C; rate of application 0.025 hbar/sec.

Figure 28 compares the strain-deformation diagrams recorded by the /12 tensile strength device during tests at 3,060° C where the load was applied at the rate of 0.025 hbar/sec. Tantalum carbide is not only superior in breaking strength but also in resistance to deformation.

Figure 29 contains the comparison at the same temperature, but where the load was applied twice as rapidly. The performances of the two materials are not as high but the difference between them is maintained.

Figure 30 shows a comparison at 2,500° C, which is the temperature of graphite at which it possesses maximum mechanical properties. Here also, tantalum carbide has without question a greater resistance to tensile stress.

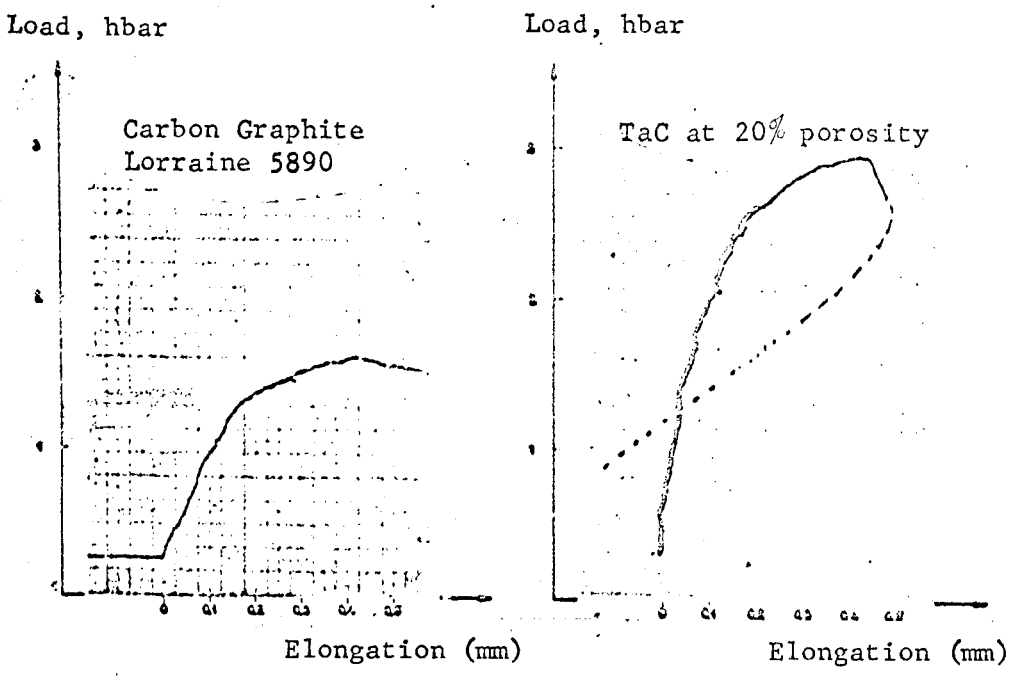


Figure 29. Diagram of strain-deformation at 3,060° C; rate of application 0.0125 hbar/ sec.

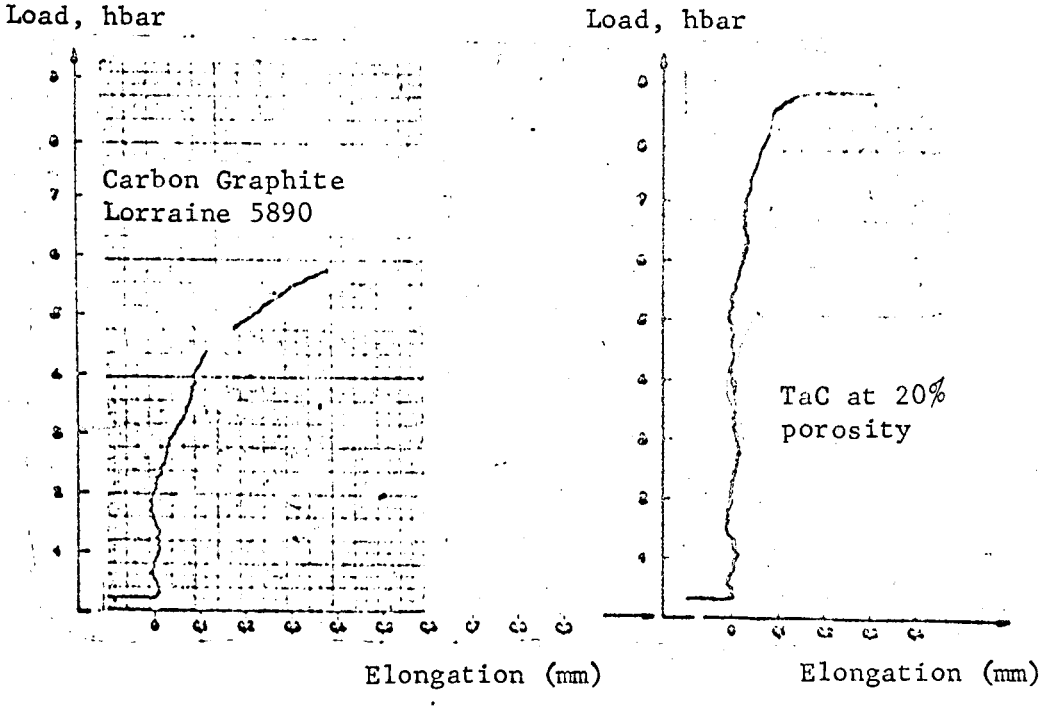


Figure 30. Diagram of strain-deformation at 2,500° C; rate of application 0.025 hbar/ sec.

Conclusion

Tantalum carbide is a refractory compound with exceptional mechanical properties at very high temperatures. However, it possesses a serious defect which would frequently make it useless in the aerospace field, i.e., sensitivity to thermal shock.

Techniques of preparing sintered fragments with stable porosity and subsequent impregnation by a metal with satisfactory thermal conductivity make it possible to overcome this handicap by conferring on the "metal-ceramic" an initial and very creditable resistance to thermal shock.

However, it must be admitted that its cost and weight speak against the use of the material. These disadvantages will necessarily narrow the range of the many possible applications. However, in difficult cases, i.e., problems regarded as insoluble, the designer would do well to consider it.

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